V.F.2 Platinum Recycling Technology Development

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Contract Number: DE-FC36-03GO13105

Subcontractors:
- DuPont, Wilmington, DE
- Delaware State University, Dover, DE

Start Date: August, 2003
Projected End Date: August, 2008

Objectives

- Develop a cost-effective and environmentally friendly technology for the recycling and re-manufacture of catalyst coated membranes (CCMs) that are used in proton exchange membrane (PEM) fuel cell systems.
- Improve ionomer-catalyst separation efficiency.
- Achieve high platinum/Nafion® catalyst recovery rate.
- Identify CCM material degradation mechanisms by characterizing end-of-life separated materials.
- Develop a re-manufactured CCM process.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(B) Cost

Technical Targets

The cost target, as it relates to our project, is a recovery rate of over 95% of the platinum group metals (PGMs) originally deployed in the new fuel cell system. Our ability to demonstrate this will allow the PGM market price to maintain stability during the initial market penetration of PEM fuel cell systems.

The durability target as it relates to our project is the demonstration of durable membranes manufactured with recovered end-of-life Nafion® membranes. This will also demonstrate the fundamental vitality of the Nafion® ionomer for durability and the nature of the impurities and failure modes of the membranes.

Accomplishments

- Developed and demonstrated a pilot-scale process to separate and purify the ionomer component of a end-of-life membrane electrode assembly (MEA).
- Demonstrated a process to re-manufacture re-covered ionomer into a new 1 mil thick fuel cell membrane using water as a solvent during the separation process.
- Operated 5 kW stack on re-cycled membrane and recycled catalyst.
- Perfected a new electrochemical catalyst activity test for oxygen reduction reaction (ORR), that uses a small amount of catalyst suspended in solution.

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Introduction

The platinum catalyst has been identified as one of the major cost contributors to the PEM fuel cell material cost structure. Currently, platinum is the most viable catalyst for PEM fuel cell systems. It is in the form of Pt-carbon-ionomer mixture coated onto the Nafion® membrane to form a CCM, or so-called MEA. The commercialization of fuel cell systems will result in an increasing demand of the PGM. Obviously, without the recycling of PGM the long-term availability of platinum becomes a serious limitation. Hence, platinum recycling is critical to the long-term economic sustainability of PEM fuel cells. Unfortunately, conventional platinum recovery processing is ill-suited for the fuel cell components due to: (1) low recovery rate of acid solvent method because the platinum particles are covered by the ionomer; (2) the presence of the Nafion® fluorine-containing polymer decomposition at high temperature results toxic and corrosive hydrogen fluoride gas released. Thus, an advanced process that enables the extraction and reuse of both the precious metal and the ionomer in current fuel cell components is under development in this project.

Approach

Ion Power researchers are developing a process that allows for the re-manufacture of new CCMs made from used CCMs extracted from failed fuel cell stacks. This will be first accomplished by removing the CCMs from the disassembled stacks, then dissolving the CCMs in an autoclave reactor to form a slurry of dissolved Nafion® together with the carbon supported platinum catalyst particles. The second step is to develop a technology that separates these two valuable ingredients and allows the Nafion® containing solution to be re-processed into a new fuel cell membrane. Ideally the recovered platinum catalyst will be re-deposited on the re-manufactured membrane so that a completely re-manufactured CCM is the final product. In order to do this, recovered catalyst and Nafion® are characterized to exam the changes of properties and structures during the component's life. The proper manufacture process will be developed based on the properties and structures of recovered materials to realize a completely remanufactured CCM. The research and development on the characterization of aged CCM material will also provide very important information to help the investigation of CCM decay and failure mechanisms that are currently hampering the performance of state-of-the-art catalyst coated membranes.

The processes will be demonstrated on the 0.1 to 10 kg scale; which represents the quantity of material required to result in enough recovered material to be introduced into the re-manufacturing process. This represents a 5 kW to 500 kW quantity of state of the art MEAs. We have developed several sources in the marketplace for this quantity of material, and have worked with the key stakeholders in the industry to demonstrate the advantages of our new approach in terms of reducing the complete life-cycle costs of fuel cell systems.

Results

We have scaled-up the process by procuring a 40 gallon autoclave reactor. We have also scaled-up our separation process as shown in Figure 1. We have a 40 gallon mixing tank to receive the contents of the autoclave reactor, then the slurry of Nafion® solution with catalyst particles is pumped around through a continuous centrifuge where the heavier catalyst particles are deposited on the walls of the centrifuge bowl. This catalyst was recovered and analyzed with our new ORR technique; see Figure 2. The linear sweep voltammetries are compared for new E-type and T-type catalysts and the recycled and recovered catalyst. The

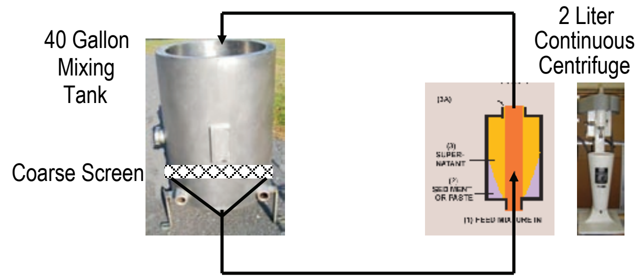

FIGURE 1. Schematic and Photo of Our Scaled-Up Separation Equipment

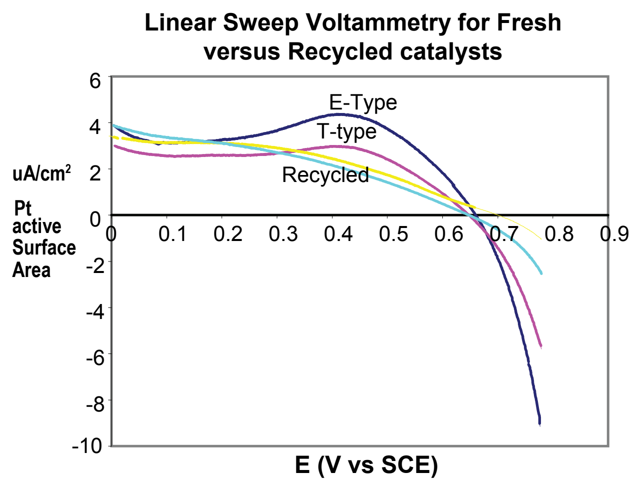

FIGURE 2. Linear Sweep Voltammetry Curves for Two Fresh types of Catalyst E and T-Type and the Recovered Recycled Catalyst

shape of the curves are different, however, the absolute signal is on the same order. This indicates that the recycled catalyst has reasonable activity. These catalysts were then used to make re-manufactured MEAs along with re-manufactured membranes. These MEAs were built into a 63 cell 280 cm^2 active area GENCORE™ 5 kW fuel cell stack system, see Figures 3 and 4. The remanufactured membrane and fresh membrane and stock MEAs all performed about the same level of performance. We have over 100 hours of run time on the stack and the membranes are still performing well. This is a good indication that the recycled and remanufactured membranes can perform well. In particular as this relates to failure mechanisms of the ionomer, it tells us that the recovered ionomer is not significantly degraded in performance as a result of the original operation.

Conclusions and Future Directions

- Recovery and separation work at scale-up has been demonstrated. Good recovery rates are being achieved.

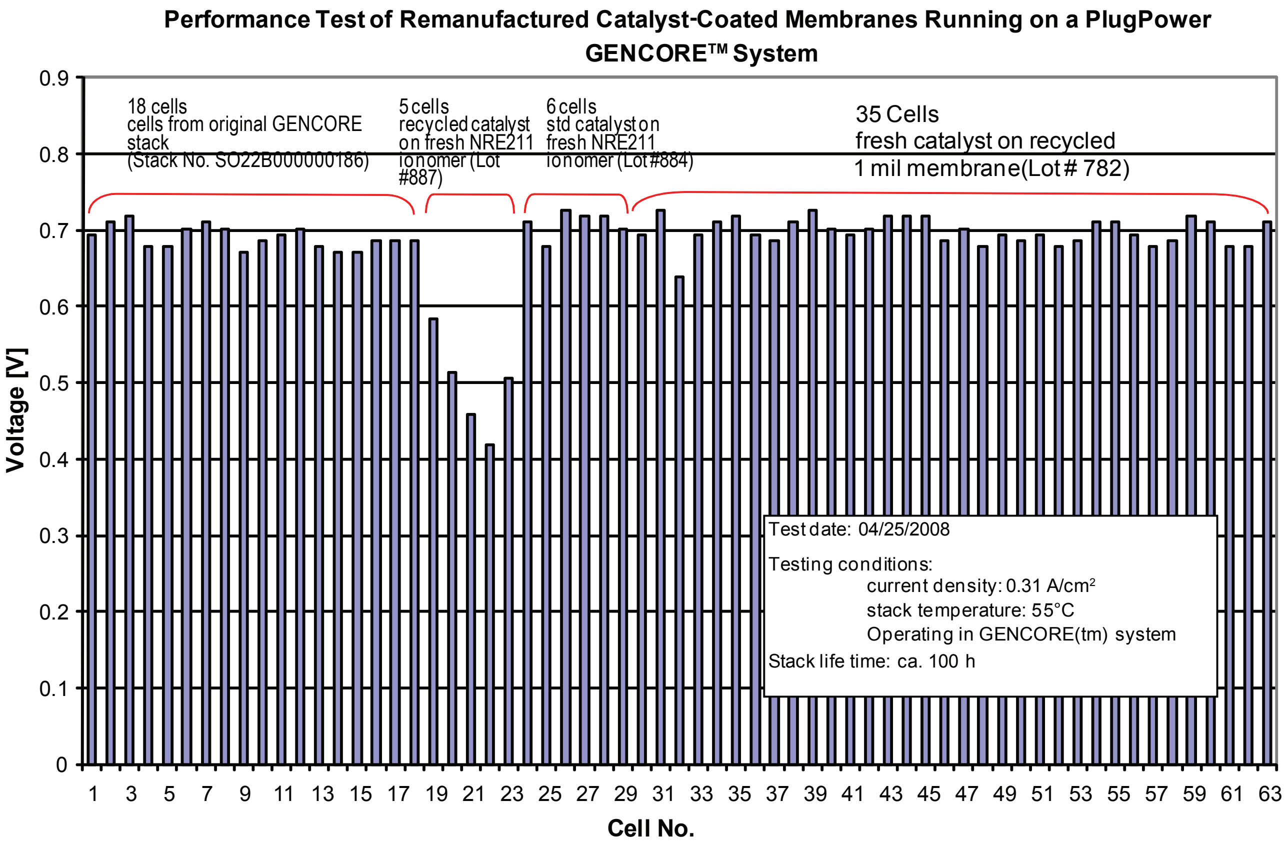

FIGURE 3. GENCORE™ System Operating on Various MEAs in the Stack

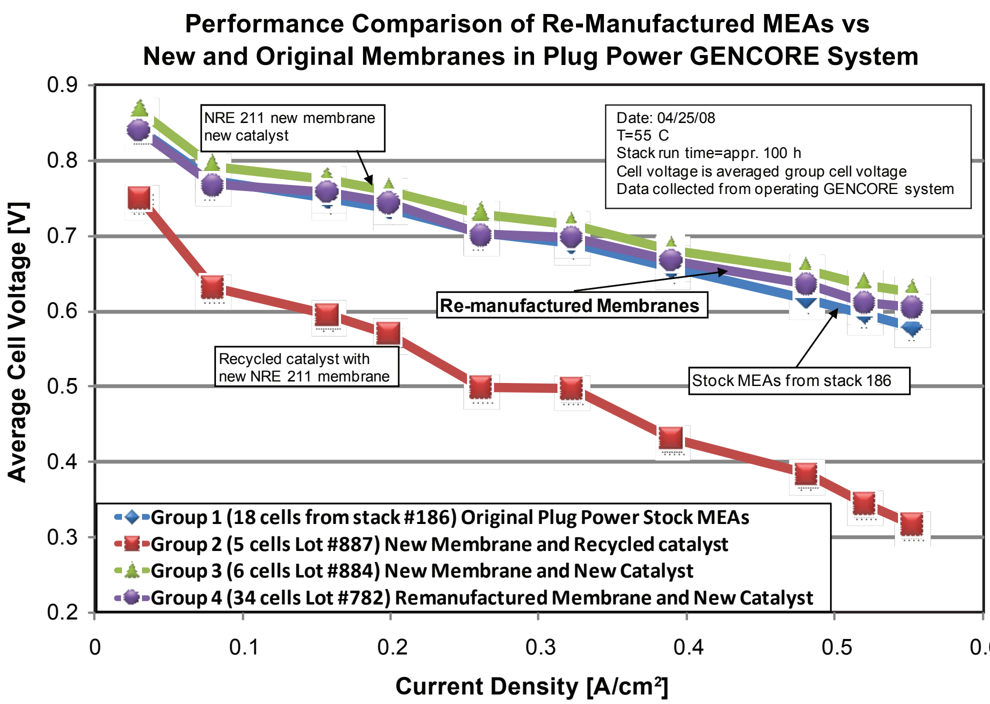

FIGURE 4. Polarization Curve of the Different MEAs Operating in the GENCORE™ System

- Recovered polymer can be re-manufactured into fuel cell membranes with performance similar to fresh membrane, thus recovered polymer is not degraded in performance.
- Effective removal of trace amounts of PGM from diffusion media needs more development.

Special Recognitions & Awards/Patents Issued

1. US Patent **7,255,798** issued Aug 14, 2007, Recycling of used perfluorosulfonic acid membranes.

FY 2008 Publications/Presentations

1. Stephen Grot, Platinum recycle Technology Development, presentation has been given to DOE review meeting, Arlington, VA, June 11, 2008.

2. K.A. Assiongbon, K. Bakayoko, A. Goudy, B. Workie, P. Hayward, Stephen Grot and Walter Grot, "Electro-catalytic activities of novel PtAg nanocatalyst for the oxygen reduction reactions in peroxide-free and peroxide containing solutions", B5 - Fundamentals of Energy Storage and Conversion, Phoenix, AZ, May 2008.

3. Hongwei Yang and Andrew Goudy, Materials Research Society Meeting (MRS), "Absorption and Desorption Kinetics of Catalyzed $NaAlH_4$ under Controlled Conditions", Boston, MA, November, 2007.

4. "Simple Electrochemical Procedure to Test the Catalytic Activity of Platinum Supported on Carbon", B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot *J. Electrochem. Soc.,* 2007 (Submitted).